

# **RHEOLOGICAL PROPERTIES OF $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ MELTS STUDY**

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## **Abstract**

Shear viscosity of p-CdTe and p-Cd<sub>0.95</sub>Zn<sub>0.05</sub>Te melts was measured by using an oscillating cup viscometer from a melting point up to 1403 K. The hysteresis of the viscosity data obtained during the heating and cooling was observed in both melts. The CdTe viscosity as a function of temperature passes through a maximum in a narrow temperature range from 1377 to 1387 K during heating with a rate of 0.33 K/min. and shows a Newtonian liquids' behavior only above 1388 K. The viscosity data of the both cooled melts can be represented by an empirical equation of the Arrhenius type. Activation energies of viscous flow are estimated as 48±1 kJ/mol for the CdTe and 66±1 kJ/mol for the Cd<sub>0.95</sub>Zn<sub>0.05</sub>Te. The obtained results are analyzed in terms of a cluster model for the melting process.

Keywords: Viscosity, CdTe, CdZnTe, melting process, clusters in a liquid, self-organization.

## **1. Introduction**

Semiconductors CdTe and  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  are widely used in research, industrial and medical applications, where large homogeneous single crystals are needed. Different techniques based on the melt directional solidification are the most suitable for the bulk single crystals growing. A melt structure influences on the process of the crystal growing from the melt [1]. However, a direct investigation of the CdTe melt's structure was performed only in [2,3] by a neutron diffraction method at 1373 K. According to the data of Gaspard et al [2,3], main structure units of this melt are small fragments of the parent crystal with zinc blend lattice, namely, the deformed tetrahedra. Nevertheless, the CdTe melt structure is unknown at higher temperatures. No information concerning direct study of CdZnTe melts structure was found in a literature, though it was shown in Ref. [4], that the  $\text{Cd}_{0.955}\text{Zn}_{0.045}\text{Te}$  crystal structure depends on the melt superheating, i.e., on the melt structure at its maximal temperature.

Experimental studies of high-temperature thermal properties of the II-VI semiconductors are very important as an indirect method of observation of structure's changes peculiarities in solid and liquid phases. However, high pressure of the components and chemical aggression of the chalcogenides essentially complicate the experimental procedures, resulting in considerable differences of published data. Even a maximal value of a CdTe melting point ( $T_m$ ) have been estimated with an essential scattering from 1365K [5] up to 1379 K [6].

The rheological properties are rather sensitive tool for investigation of the melt structure rearrangement. Earlier a temperature dependence of CdTe's viscosity was studied by Glazov et al [7] and Lopatkina et al [8], but their data differ more than twice, especially near  $T_m$ . Analyzing the obtained monotonous diminution

of the viscosity from 1373 K to 1473 K, it was concluded in [8] that the viscous flow activation energy had been reduced approximately twice at 1413 K.

We have compared temperature dependencies of the shear viscosity in  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  and  $\text{CdTe}$  melts, investigated during the heating up to 1403 K followed by cooling and holding at different temperatures.

## **1. Experimental procedure**

$\text{CdTe}$  and  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  samples were prepared from pure elements (6N grade) in evacuated and sealed quartz standard cups for viscometer. After melting, the samples were homogenized during 12 hours at 1423 K and cooled with the furnace. A free volume above the melts reached 50 – 60 %.

The shear viscosity was measured quasi-uninterruptedly using the computer controlled cup viscometer similar to [9]. Using an equation proposed by Roscoe [10] the viscosity has been calculated from the logarithmic decrement and the period of oscillations. The temperature was measured by a Pt-Pt/Rh thermocouple, arranged just below the cup and calibrated by measuring the viscosity of pure (5N) Pb, Sb and Ag at their melting points. As a result, an accuracy better than 0.5 K in the whole temperature range was achieved. Experimental data were obtained during a heating (cooling) with rates of  $V_{h/c} = 0.33 \text{ K/min}$  for the molten  $\text{CdTe}$  and  $V_{h/c} = 0.17 \text{ K/min}$  for the  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$ .

## **1. Results and discussion**

### **1.1 CdTe**

Experimental data on the period of oscillations as a function of a temperature  $P(T)$ , presented in Fig. 1, illustrate a gradual nature of a  $\text{CdTe}$  melting process.

According to Fig. 1, a liquid phase appears really at  $T_m = 1365$  K that verified this commonly used [5] value. Further heating of the charge, obviously, is resulted in a smooth increase of the liquid phase volume fraction up to 1378 K where the rapid structural changes in a rather narrow temperature range occurs. The change of  $P(T)$  slope should correspond to the change of dominated structure units' composition and/or configuration up to the temperature of second change of  $P(T)$  course (at 1385 K), where the  $P(T)$  slope is reproduced. An overheating of the melt above 1385 K is resulted in  $P(T)$  exponential decreasing down to 1388 K. A melt structure reached at 1388 K, is probably more equilibrated in comparison with previous state, since it is fully reproduced in a temperature region from 1388 to 1403 K both during the heating and cooling. Therefore, three critical points ( $T_{c,1} = 1378$  K,  $T_{c,2} = 1385$  K and  $T_{c,3} = 1388$  K) had limited three different states of the CdTe melt during the heating at given conditions.

The melt cooling from 1388 K with the same rate does not reproduce the rheological properties of the system that is resulted in a hysteresis occurrence. Even 80-min. holding of the cooled melt at  $T_{c,3}$  did not provoke any changes towards the state, which had been observed between  $T_{c,1}$  and  $T_{c,2}$  during melt heating. Contrary, the next holding at  $T_{c,1}$  showed a tendency to the state reproduction (structure and/or composition), which was reached at the same temperature during the heating. Nevertheless, the melt structure and viscosity remain almost stable during the holding just before  $T_m$ , namely, at 1367 K. Moreover, the latter did not facilitate the solidification process which occurred with undercooling.

Based on experimental data, the calculated temperature (Fig. 2) and time (Fig. 3) shear viscosity dependences confirmed this considerations and illustrated them more

visible. So, one can see that  $\eta(T)$  dependence passed through a maximum, and only then exhibited typical for Newtonian liquids behavior. Similar “anomaly” had been observed in some others molten semiconductors, partly, in  $\text{Ga}_2\text{Te}_3$  and  $\text{In}_2\text{Te}_3$  [7,11,12], which have the same type of the lattice (zinc blend). Tsuchiya et al [11,12] explained this effect on the base of a double-structure model, regarding, that dominated near  $T_m$  “a low-temperature structure” retains features of parent crystal and “a high-temperature structure” is more densely packed, presumably of a linear type (chains or molecules).

Recently a fundamental model of molten CdTe structure based on first principles, performed by Godlevsky, Chelikovsky, Derby in [13,14] was published. According to their calculations, a heating of CdTe much above  $T_m$  leads to substantial structural changes with a transformation to a more close-packed atomic structure. Besides, they found that atoms of Te form infinite branched chains near the melting temperature. As the temperature increases, the chains break, become shorter and transform to close-packed clusters, which are rather stable in the superheated state.

Tacking into account this model, the peak in the  $\eta(T)$  dependence of the heated melt (Fig. 2) can be attributed to the Te atoms branched chains formation. According to the  $\eta(T)$  data, this structurization of the melt occurred in rather narrow temperature range followed by the chains decay on smaller species. Probably, this process takes place preferably during the melt heating because we did not find the conditions (temperature, time of holding) of such type complexes reproduction during the cooling of the melt superheated up to 1403 K. Shown in Fig. 3a, the viscosity as a function of the holding time at  $T_{c,3} = 1387.4 \pm 0.1$  K illustrated small (from 3.15 up to 3.20 mPa·s ) changes of the viscosity, which correlated with temperature fluctuations. Such correlation reflects certain stabilized state of the melt structure units at this temperature.

The scatter of the viscosity from 0.67 to 0.71 mPa·s during the holding at  $1367.5 \pm 0.1\text{K}$  (Fig. 3b) had its own internal regularity, probably, due to the components diffusion between equilibrated adjacent phases. The most remarkable in these experiment the changes of the viscosity, which observed during the holding at  $T_{c,2}$  (Fig. 3), can be described by exponential function that gave evidence of a self-correlation in the melt. Similar to Fig. 1, this kinetic curve demonstrates that long time is needed for complete relaxation of the melt structure.

It seems to be interesting to compare the  $\eta(T)$  dependence of the cooled melt with the Arrhenius-type equation for monoatomic Newtonian liquids

$$\eta(T) = \eta_0(T) \exp(-E_a/RT) \quad (1)$$

where  $\eta_0$  is a constant,  $R$  is the ideal gas constant,  $E_a$  is the energy of activation of viscous flow (EAVF).

It is known, that a mechanism of viscous flow is defined by two main factors: energetic and dimensional. The EAVF of a simple liquid is defined by creation of a vacancy and replacement of the unit of viscous flow into the vacancy. Thus, the EAVF reflected the energy of the viscous flow units interaction.

Using the data of  $\eta(T)$  of the cooled from 1403 to 1387 K melt, the energy of activation estimated from eq.1 is  $E_a = 48 \pm 1 \text{ kJ/mol}$ . This value is comparable with the energy of activation of chemical reactions. It means, that even this cooled melt is associated. For replacement into a neighbor vacancy, an atom from associate should obtain additional energy of sharing stress, reasonable for break of the bond.

Given in Figs.1-3 data confirms a conclusion, based on differential thermal analysis (DTA) results in [15-17] that CdTe melting process occurs in some temperature range above  $T_m$ . Revealed by DTA a small additional endothermic effect at 1373 K

completed the transformation of crystal-like clusters into the liquid. It was supposed in [16,17] that the clusters dissolution occurs mostly by fragmentation from  $T_m$  to  $T_m + 5$  K, above this point up to  $T_m + 10$  K the clusters dissolve from the surface. As is clear from Figs. 1 and 3, the change of the slope of both dependencies on temperature also occurs at  $T_m + 5$  K.

Shown in Fig. 2 data give a possibility to determine the clusters volume fraction dependence on temperature (see set in Fig.2). The data illustrate that the clusters' content becomes a minimum one near  $T_m + 10$  K or  $T_{c,1}$ . According to the data in the Figs. 1 and 2, certain intermediate structure of the heated melt exists between  $T_{c,1} = 1378$  K and  $T_{c,2} = 1388$  K. Probably, the created as result of the clusters dissolution the smallest fragments of the lattice, namely, the tetrahedra [2,3] turn in such way that infinite Te branched chains [13,14] form. However, exact determination of the clusters rearrangement needs further direct investigation.

### 3.2. $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$ .

Phase diagram of the CdTe – ZnTe system (a type of “cigar”) assumed unisothermal melting process of the solid solution of any composition. Fig. 4 illustrates the expected hysteresis of the period of oscillation and the viscosity as a function on temperature. According to Fig. 4, the  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  a melting process started at 1380 K and finished near 1395 K, where the melt reached a more equilibrium state. Contrary to CdTe, the melt structure rearrangement during the heating occurs in less expressive manner. The introduction of 5 at.% of isovalent relatively to cadmium impurity is resulted in the increase of the viscosity value of the cooled melt from 3 to 4 mPa·s. This



fact is correlated with the rise of EAVF to  $E_a = 66 \pm 1$  kJ/mol in the 1400 – 1387 K temperature range.

Tacking into account that the  $\eta(T)$  slope changed at  $T_m + 5$  K, one can suppose that, similar to CdTe case, the clusters dissolution mechanism is changed in this point. In such case, the small peak at 1387 K can be attributed to the tetrahedra complete “release” followed by their aggregation due to Coulomb forces. These interactions balance against thermal forces and external influences such as gravity to determine what configurations the particles will adopt. As a result of such self-organization, a three-dimensional structure might be created that caused the viscosity rise. Comparing the curves of the cooled melts, one should conclude that the created structure is more stable in the Zn presence than in pure CdTe, though the anomalous peak had been observed in the heated CdTe melt.

According to the Fig. 4, a homogeneous nucleation of the  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  melt similar to the CdTe begins near the temperature of the first rapid rearrangement of the heated melt structure, i.e. at  $1388 \pm 1$  K. One of the possible explanations of this coincidence is the fact that the main structure “units – tetrahedra” makes a correlated turning in this point both during the heating and the cooling. The nucleation process of  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  melt is completed by full solidification at 1371 K.

## 1. Conclusion

The shear viscosity measurements give the possibility for monitoring the melting and solidification processes of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  melts. It was revealed that a fine structure of binary and ternary compounds’ melting process differs, though it can be explained in the framework of the cluster model of the melting process in both cases. The presence of 5

at.% of the isovalent doping zinc in the CdTe lattice not only increases the melting point of CdTe, but maintains the melt viscosity values from 3 to 4 mPa·s and the activation energy of the viscose flow from 48 to 66 kJ/mol.

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## FIGURE CAPTIONS

Fig. 1. Period of oscillations measured for CdTe as a function of temperature.

Fig. 2. CdTe shear viscosity dependence on temperature. In set: the volume fraction of the clusters in the CdTe melt as function of temperature.

Fig. 3. CdTe melt shear viscosity dependence on time of the holding at  $1387.4 \pm 0.1$  K (a), at  $1377.4 \pm 0.1$  K (b) and  $1367.4 \pm 0.1$  K (c).

Fig. 4. The period of oscillations (a) and viscosity of  $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$  melt vs temperature.

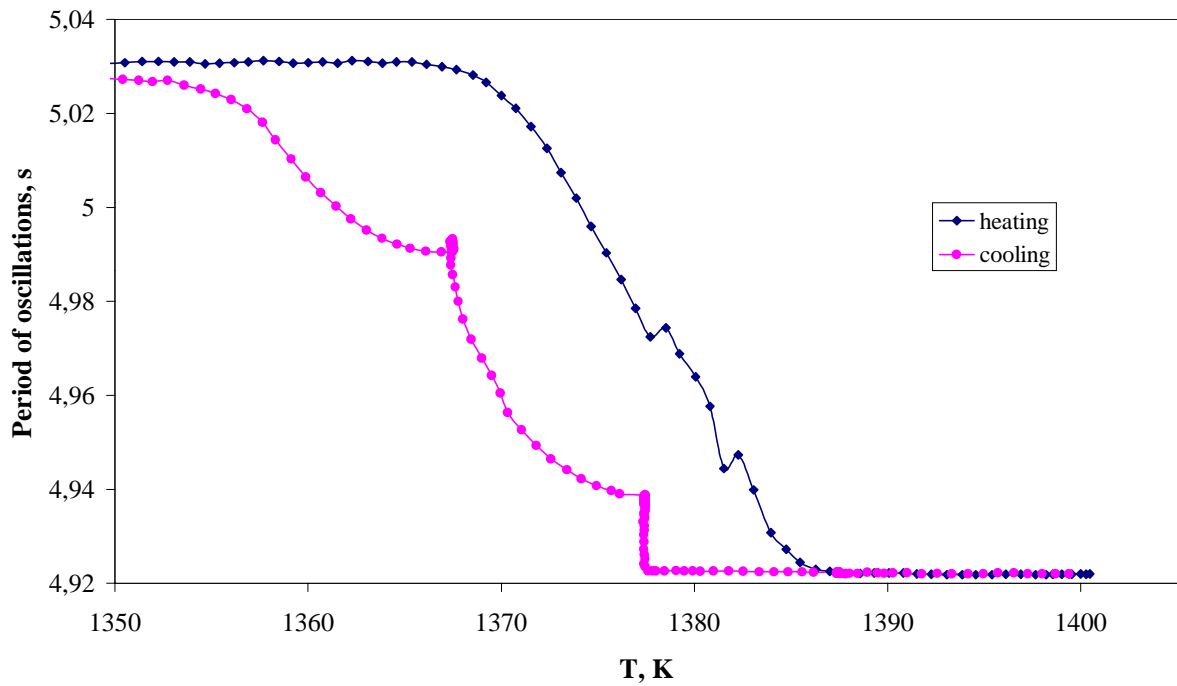


Fig.1.

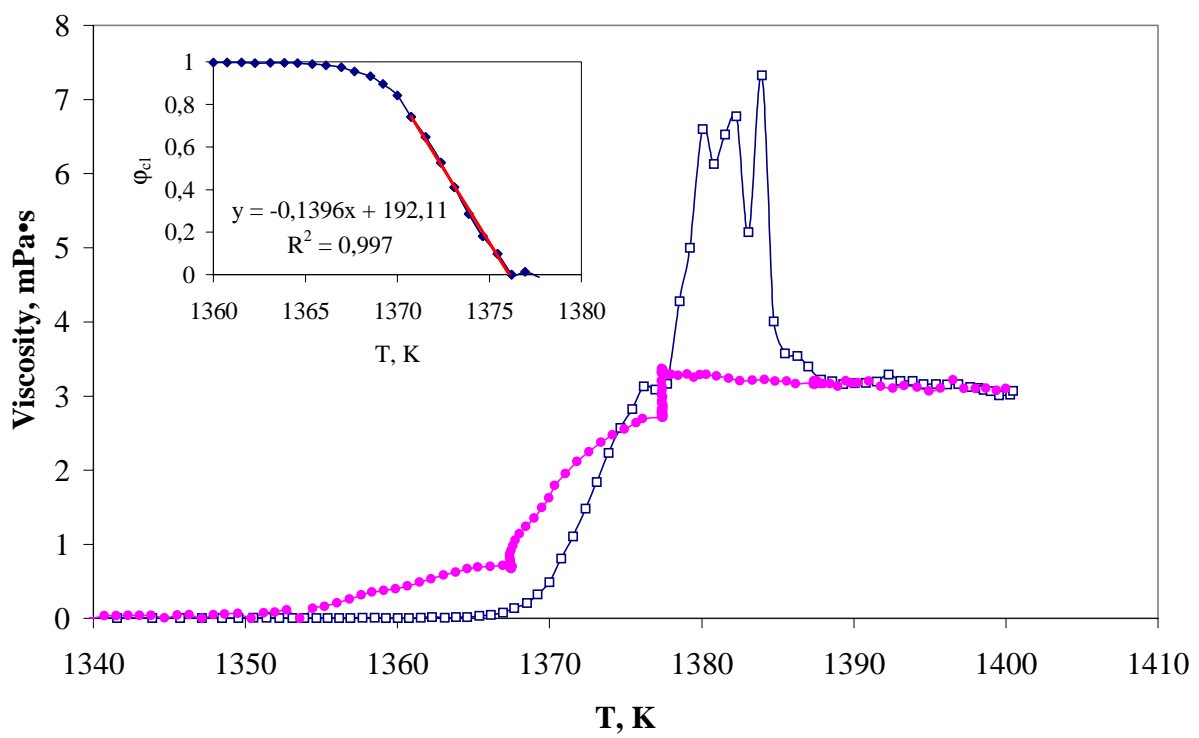


Fig.2.

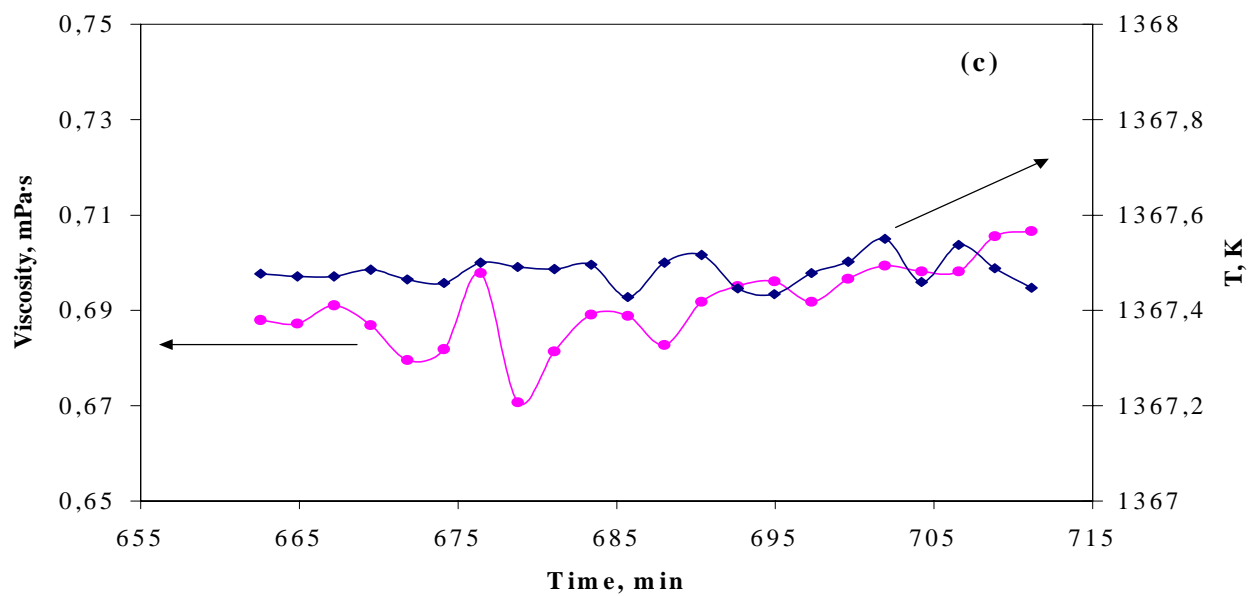
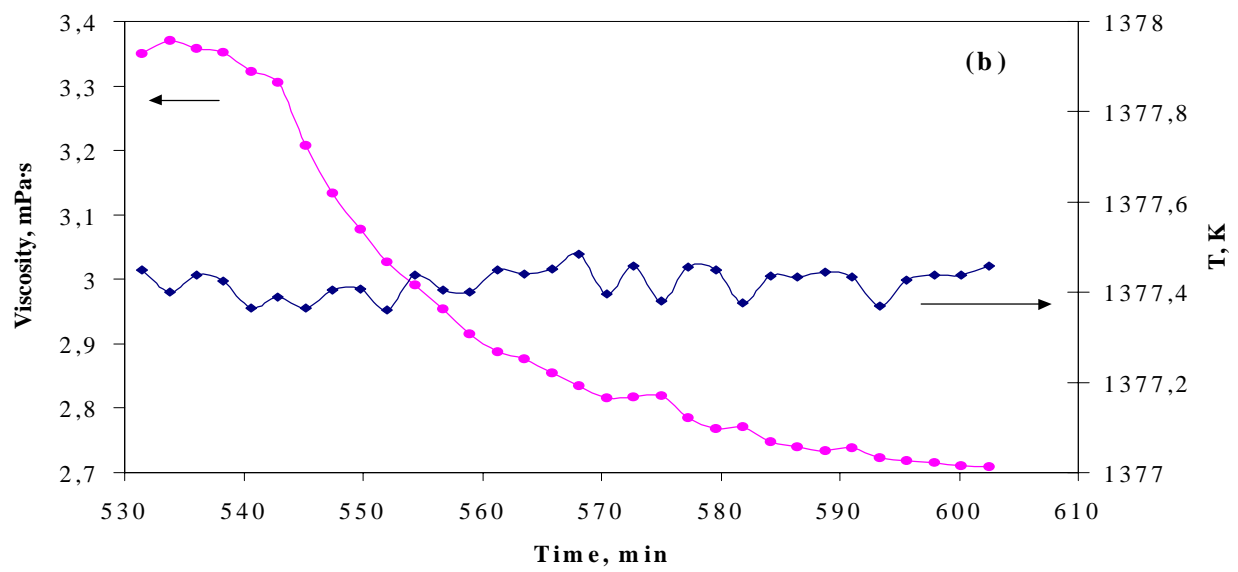
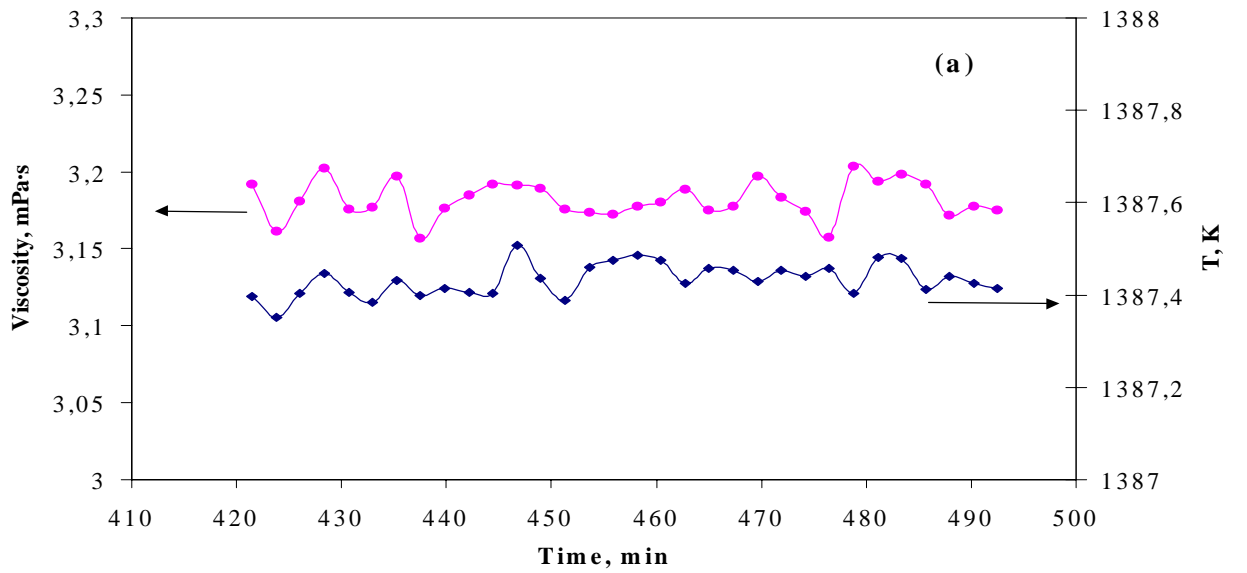


Fig.3.

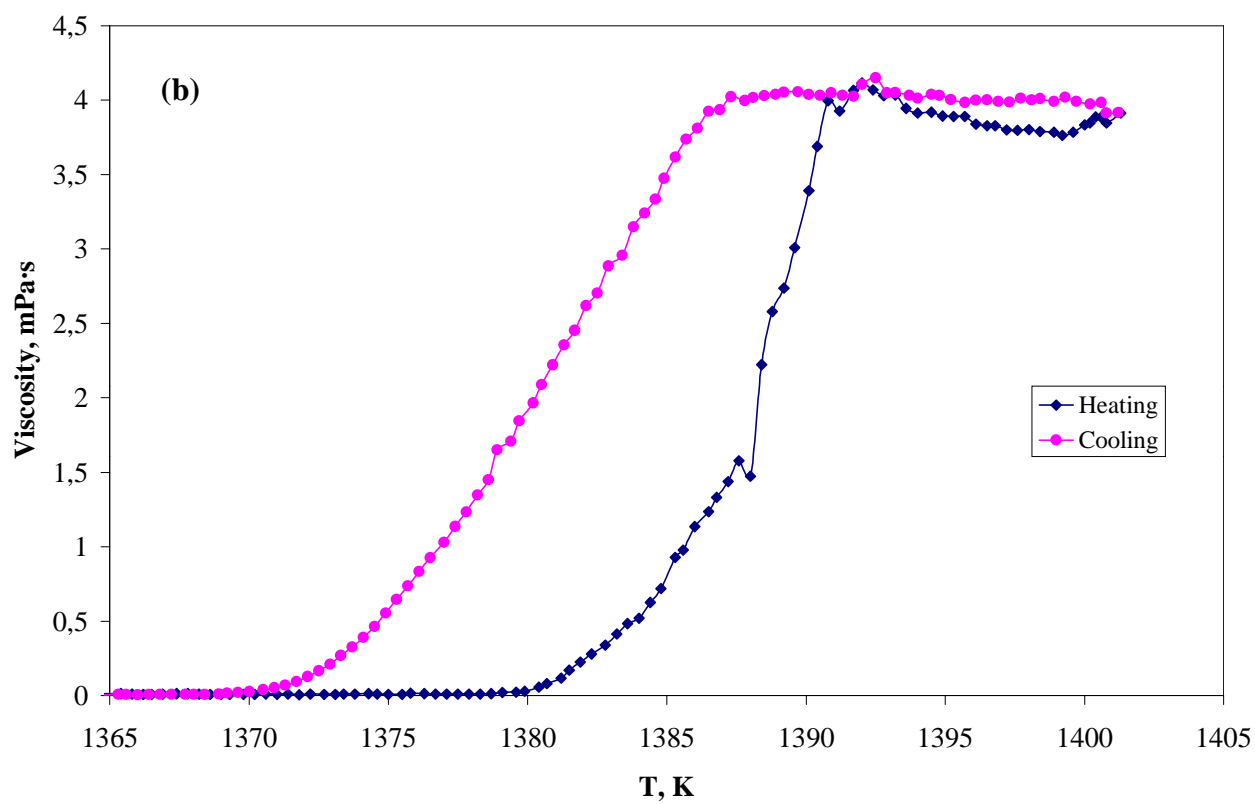
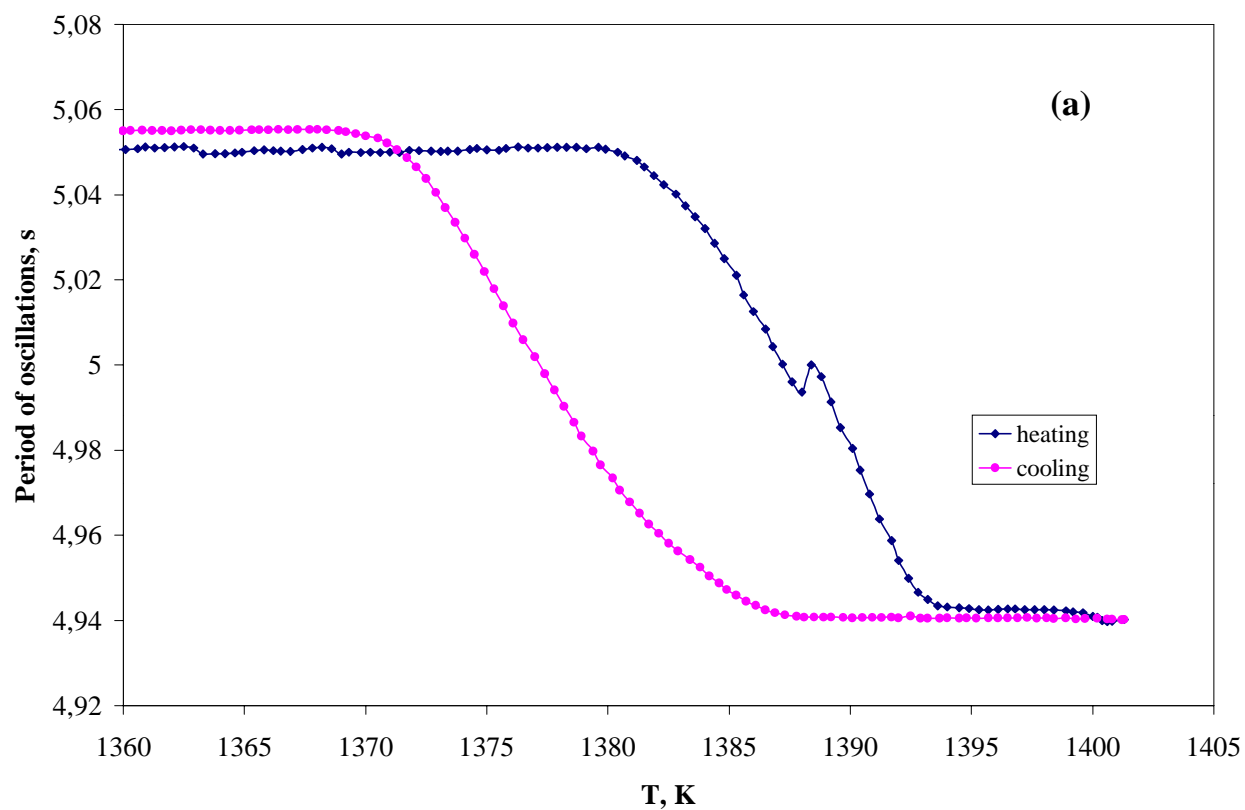


Fig.4.